Charge Mobility and Recombination Mechanisms in Tellurium van der Waals Solid

Prashant Bhaskar,* Alexander W. Achtstein,† Martien J. W. Vermeulen, and Laurens D. A. Siebbeles*‡

Optoelectronic Materials Section, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands

ABSTRACT: Trigonal tellurium is a small band gap elemental semiconductor consisting of van der Waals bound one-dimensional helical chains of tellurium atoms. We study the temperature dependence of the charge carrier mobility and recombination pathways in bulk tellurium. Electrons and holes are generated by irradiation of the sample with 3 MeV electrons and detected by time-resolved microwave conductivity measurements. A theoretical model is used to explain the experimental observations for different charge densities and temperatures. Our analysis reveals a high room temperature mobility of $190 \pm 20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The mobility is thermally deactivated, suggesting a band-like transport mechanism. According to our analysis, the charges predominantly recombine via radiative recombination with a radiative yield close to 98%, even at room temperature. The remaining charges recombine by either trap-assisted (Shockley–Read–Hall) recombination or undergo trapping to deep traps. The high mobility, near-unity radiative yield, and possibility of large-scale production of atomic wires by liquid exfoliation make Te of high potential for next-generation nanoelectronic and optoelectronic applications, including far-infrared detectors and lasers.

INTRODUCTION

Extensive studies on fundamental properties of two-dimensional (2D) van der Waals materials have revealed new possibilities for the development of next-generation optoelectronic devices.1–8 Two-dimensional materials, where layers of strongly bound atoms are weakly held together by van der Waals forces, exhibit the possibility of separating the layers via exfoliation techniques, allowing one to engineer their electronic and optical properties. Similar to 2D materials, in one-dimensional (1D) materials, covalently bound chains of atoms are held together by weak van der Waals forces in the two perpendicular directions. Such 1D materials also have interesting promising applications in nanoelectronics. Two such impeccable 1D systems are trigonal selenium (Se) and tellurium (Te), which have crystal structures that consist of helical chains of atoms. These materials exhibit potential for various applications due to their stability in air. As proposed for Se,9 exfoliation of bulk Te to obtain 1D atomic chains of Te has been demonstrated recently.10 However, Te is different from Se because of strong interchain electronic coupling in the bulk, thus being a quasi-1D system.11 In addition, the 0.33 eV band gap of Te12,13,14 is much lower than the 1.9 eV band gap of Se.15

As a 1D van der Waals material, Te has been widely studied for its electronic structure,3–6 optical properties,12,13,14 Hall conductivity, and extrinsic mobility in p-type Te.18–21 Very recently, it gained attention due to its high thermoelectric figure of merit.22,23 The aforementioned studies on conductivity and mobility have mostly been performed at low temperatures (∼77 K),20 with externally doped samples and using contact measurements.20,24 Therefore, it is of great interest to study its intrinsic optoelectronic properties without external doping and at temperatures close to ambient.

In the present investigation, we provide insights into temperature-dependent intrinsic charge carrier mobility and decay mechanisms in trigonal Te with varying charge carrier density, building upon our earlier results on other van der Waals materials.7,15,18 Quantitative analysis of our experimental observations reveals the characteristics of charge carrier mobility and recombination in the quasi-1D atomic chains of Te in bulk, laying the basis for further investigations of exfoliated Te. The high mobility and near-unity quantum yield (QY) make Te of interest for nanoelectronics and optoelectronics. These properties and the low band gap make Te a promising material for use in far-infrared detectors. The appreciably high mobility and quantum yield result in low device resistance and 1/f noise, which are essential to realize a high S/N ratio.26

EXPERIMENTAL METHODS

Te pellets with purity 99.999% were procured from Sigma-Aldrich (now MERCK) and used as received without any...
Further treatment. Te pellets were finely powdered using a mortar and pestle for studying contactless microwave conductivity at various temperatures and at various densities of excess electrons and holes. The microwave conductivity studies were performed at frequencies in the range of the K band (27–38 GHz), similar to our previous studies. Uniform densities of excess electrons and holes were generated by irradiation with 3 MeV electron pulses from a van de Graaff accelerator, along with Bremsstrahlung irradiation, which was produced by retarding the electron pulses by a 2 mm lead (Pb) sheet. The high-energy Bremsstrahlung photons generate electron–hole pairs along their paths through the sample. Successive irradiation of the sample had no effect on the transient conductivity, implying the absence of radiation-induced damage.

The powdered Te sample was filled into a polyether-etherketone (PEEK) sample holder with a groove of 1 mm along the direction of high-energy irradiation. In this sample holder, the sample height along the direction of electron irradiation is 1 mm, whereas the sample holder size is close to 3.5 mm. Such a sample holder was designed to avoid nonuniform generation of charges, as would have occurred because of stopping of high-energy electrons within the sample, discussed next. As tellurium is a heavy material, with atomic number $Z = 52$, density $\rho_{Te} = 6.2$ g cm$^{-3}$, and $M_{Te} = 127.60$ g mol$^{-1}$, it exhibits a comparatively higher stopping power ($S(E) = -dE/dx$) for the 3 MeV electrons, as compared to materials we studied previously. A higher stopping power leads to lower average penetration depth ($\Delta x$) for the 3 MeV electrons in the sample, which leads to a nonuniform distribution of charges inside the sample. To avoid a nonuniform charge density, the sample height was reduced so that the high-energy electrons could pass through the sample, generating a close to uniform distribution. The stopping power and average penetration depth values were calculated using eqs 1 and 2, respectively, which were obtained by simplifying Bethe’s expression for the collisional mass stopping power (also known as linear energy transfer) for high-energy electrons:

$$\left( S \right)_{Te} = \left( \frac{S}{\rho} \right)_{H_2O} \frac{18}{10} \frac{\rho_{Te}}{M_{Te}} \frac{Z_{Te}}{E}$$

$$\Delta x = \int_0^{E_0} \frac{1}{S(E)} dE$$

In eqs 1 and 2, $\rho$ is the mass density, $Z$ is the atomic number, $M$ is the elemental or molecular weight, and $E_0$ is the 3 MeV energy of incident electrons. Equations 1 and 2 yield an average penetration depth of 3.5 mm. Because this significantly exceeds the sample width of 1 mm, a uniform density of electrons and holes is produced upon irradiation.

The stacked two-layered structure consisting of Te and PEEK sample holder results in a heterogeneity of the sample along the direction of irradiation. In such a case for studying microwave absorption, the effective dielectric constant of a heterogeneous sample can be estimated by considering the Maxwell–Wagner effect, which is described by:

$$\varepsilon_\ast = \varepsilon_\ast' - j\varepsilon_\ast'' = d \left[ \sum_i \frac{d_i \varepsilon_i'}{d_j \varepsilon_j'} \right]^{-1}$$

In the above equation, $d$ is the total height of the layered sample, $d_j$ is the height of the $j$th layer, $\varepsilon_j'$ ($\varepsilon_j''$) is the real (imaginary) part of the permittivity of the $j$th layer, $\varepsilon_\ast'$ corresponds to the effective dielectric constant and $\varepsilon_\ast'' = -1$. This effect introduces a sensitivity factor $B$, which is used to obtain the conductivity in absolute values (discussed below).

Because of very high conductivity signals of Te, nearly saturating the electronic regime of the experimental setup, even for a short electron pulse duration of 500 ps, the radiation dose was reduced by using a 2 mm Pb plate placed at the top of the experimental cell containing the sample. The introduction of the Pb plate resulted in a reduction of the irradiation dose by 70 times because of partial stopping of 3 MeV electrons in the plate and production of Bremsstrahlung. The reduction factor was deduced from a test experiment of Te using 300 ps electron pulse with and without using a Pb plate, for which the conductivity signal was well within the saturation range. The final dose on the sample is a result of slowed down electrons as well as Bremsstrahlung. The incident high-energy electrons together with the Bremsstrahlung resulted in the formation of uniformly distributed electrons and holes in the sample with number density $G$ per unit time. $G$ is given by the ratio of the known energy-transfer rate (radiation dose per unit time) from the irradiation and the energy required for the formation of an electron–hole pair.

The radiation dose in Te, $D_{Te}$, was obtained from a reference measurement on benzene (Bz), which was found to be $530$ J m$^{-2}$ nC$^{-1}$, according to $D_{Te} = D_{Bz}(N_{Te}\rho_{Te}M_{Te}/N_{Bz}\rho_{Bz}M_{Bz})$, followed by a reduction of 70 times due to the Pb sheet, where $N_i$, $\rho_i$, and $M_i$ are the number of the electrons per atom/molecule, mass density, and atomic/molecular mass for Te or
The total electron or hole density is \( n_i(t) = n_i + \Delta n_i(t) \) (and \( n_h(t) = n_h + \Delta n_h(t) \)), where \( \Delta n_i(t) \) and \( \Delta n_h(t) \) is the density of excess electrons or holes produced by the incident high-energy irradiation. Note that the initial excess densities are equal, i.e., \( \Delta n_i(t) = 0 \) = \( \Delta n_h(t) \). Further, the first term describes the generation of electrons and holes with a rate \( G_{\text{pulse}} = G(\Theta(t) = -\Theta(t - t_{\text{pulse}})) \), where \( \Theta \) is the Heaviside function making the expression nonzero only during the high-energy irradiating pulse with duration \( t_{\text{pulse}} \). Furthermore, \( \phi_{ni} \) and \( \phi_{nh} \) denote the fraction of initially generated charges surviving from direct trapping or geminate electron–hole recombination during the 3 MeV electron pulse. Terms containing the factor \( n_i^\ast \) take into account the generation of electron–hole pairs by deviation from the thermodynamic equilibrium carrier density \( n_i \) through absorption of blackbody radiation, thermal excitation, or impact ionization by sufficiently energetic intrinsic thermally excited charge carriers. The intrinsic density of charge carriers is given by

\[
n_i = \left( \frac{m^*_e m^*_h}{\pi \hbar^2} \right)^{3/2} e^{-E_g/2k_BT} \quad \text{for a three-dimensional (3D) semiconductor,} \]

with \( m^*_e \) and \( m^*_h \) being the effective masses of electrons and holes taken from previous reports, respectively.\(^{12,15}\) Furthermore, \( k_B \) denotes the Boltzmann constant, \( T \) the temperature, and \( \hbar \) the reduced Planck constant. Note, that Liu et al.\(^{11}\) reported that the interchain electronic coupling of Te atomic wires is comparable to the intrachain electronic coupling. This causes Te to behave almost like an isotropic 3D system rather than a 1D system such as Se, so that the use of the 3D intrinsic carrier density above is substantiated.

The second terms in eqs 4 and 5 take into account trapping and subsequent nonradiative electron–hole recombination according to the Shockley–Read–Hall (SRH) model,\(^{38}\) neglecting defect parameters (the densities of electrons and holes in case the Fermi energy coincides with the trap level\(^{10}\)). The parameters \( k_{\text{SRH}} \) and \( k'_{\text{SRH}} \) denote the trapping rate constants for SRH recombination. In an ideal case, they are proportional to the trap density and electron- and hole-capture coefficients, which depend upon the thermal velocity of the charges.\(^{11}\) However, the temperature dependence of trapping rate constants may, nevertheless, deviate from the ideal case, e.g., when trapping processes are thermally activated. The third terms in eqs 4 and 5 represent charge trapping with the characteristic rate \( k_n \) (and \( k_h \)), which by themselves yield a stretched-exponential (quasi-exponential or Kohlrausch)\(^ {32}\) decay given by

\[
n(t) = n(t = 0) e^{-\beta t} \quad \text{for } n(t) = n_i + \Delta n_i(t) \quad \text{and } \Delta n_h(t) = 0,\]

where \( \beta \) is a parameter that characterizes dispersive charge diffusion in an exponential energy landscape. For an exponential distribution
of trap site energies of width $k_B T_0$, the $\beta$ parameter is given by $\beta = T/T_0$.\textsuperscript{35,45–47} The fourth terms in eqs 4 and 5 account for radiative recombination of an electron–hole pair with rate coefficient $k_r = pE^2/(k_BT)^{3/2}$, with $p$ as a constant independent of temperature.\textsuperscript{5,41} The decrease of $k_r$ with temperature is understood in terms of the decreasing likelihood of matching equal but opposite momenta of free carriers, imposed by momentum conservation during recombination, as the average thermal energy and hence Fermi vector increases with temperature.\textsuperscript{48}

Temperature-Dependent Electron and Hole Mobility and Decay Rate Coefficients. Figure 1 shows that the theoretical model, given by eqs 4 and 5, reproduces the measured transient conductivities. The fitted parameters, combined electron and hole mobility ($\mu_{n1} + \mu_{n2}$), band-to-band radiative recombination ($k_r$), Shockley–Read–Hall rate constants ($k_{n1}^{SRH}$ and $k_{n2}^{SRH}$), and characteristic rate constants for stretched exponential decay of charges ($k_{n1}$ and $k_{n2}$) are shown in Figure 2 as a function of temperature. The trapping rates for electrons and holes cannot be distinguished, as they are interchangeable. In our previous work on Se, electrons and holes could be distinguished because it was known from literature that electrons are trapped faster than holes.\textsuperscript{5,49} Such information is not available for Te and consequently we cannot distinguish electrons and holes. Hence, the charge carrier densities and related rates and mobilities are denoted as $n_1$ for one type of charge and $n_2$ for the counter charge. As mentioned earlier, the numerical fits were found to reproduce the experimental results only for the calculated intrinsic density valid for a three-dimensional system and not for a one-dimensional system, in agreement with the finding of Liu et al.\textsuperscript{11} Additionally, the numerical fits could only reproduce the experimental data by taking the values for the initial yield of charges ($\phi$ in eqs 4 and 5) equal to unity. This implies that the initially generated charges do not undergo geminate recombination to form excitons, as could be expected because the exciton binding energy in Te is only 1.2 meV.\textsuperscript{13} Furthermore, the charges are generated far apart in the sample, larger than the critical escape radius determined by the thermal energy.

The mobility obtained at room temperature is 190 ± 20 cm$^2$ V$^{-1}$ s$^{-1}$. This value is somewhat lower than the values near 700 cm$^2$ V$^{-1}$ s$^{-1}$ reported for thin layers of 1D and 2D Te nanostructures in field-effect transistors (FETs).\textsuperscript{54,50} The latter values can be higher than ours due to enhancement of the mobility for thinner samples\textsuperscript{50} and/or due to the high charge density in field-effect transistor (FET) measurements resulting in filling of trap states. The high mobility in Te may be in part due to the absence of polar optical phonon scattering, which significantly limits the mobility in compound 2D semiconductors.\textsuperscript{51} Figure 2a depicts that the combined electron and hole mobility decreases with temperature, which is typical for band-like transport. This can be because of the combined effect of various types of electron–phonon scattering processes. Classically, ionized impurity scattering of charges generally occurs because of elastic scattering of charges with ionized shallow-donor impurities in a semiconductor. Because of this scattering, the mobility is expected to increase with $T^{3/2}$ at low temperature.\textsuperscript{41} Ionized impurity scattering leads to increase in mobility with temperature, which can be a reason for the initial flatness in the mobility trend up to 200 K together with another process decreasing the mobility with temperature. Above 200 K, the mobility decreases because of electron–phonon scattering. The observed decrease in the mobility with temperature in Te is in line with the trends in previous reports.\textsuperscript{50,23}

Figure 2b shows the temperature dependence of the second-order band-to-band radiative recombination rate constant ($k_r$), which decreases with temperature, as expected from theory (see Theoretical Model of Charge Carrier Generation and Decay Dynamics section). The numerical fits to the experimental data in Figure 1 yield a room temperature value of $k_r$ equal to $(1.1 \pm 0.1) \times 10^{-8}$ cm$^3$ s$^{-1}$. In the case of diffusion-limited radiative recombination, the rate constant would be related to the combined mobility of charges according to $k_r = c(\mu_{n1} + \mu_{n2})/\varepsilon_0 F_r$. Taking $\mu_{n1} + \mu_{n2} = 190$
The Journal of Physical Chemistry C

Article

cm$^2$ V$^{-1}$ s$^{-1}$, $\epsilon = 28.8^{52}$ the recombination rate for the diffusion-limited $k_d$ is then estimated to be $1.2 \times 10^{-5}$ cm$^3$ s$^{-1}$, which is almost 3 orders of magnitude higher than the value obtained from the fitting. Therefore, the radiative recombination in Te is concluded to be a reaction-limited process, rather than a diffusion-limited process.

Figure 2c,d show the temperature dependence of trap-assisted SRH rates, as well as rates to trapping of charges into an energetically exponential distribution of trap sites. Incorporation of two pathways for charge decay via trapping is the result of the inability to reproduce our experimental data with either type of processes individually. SRH mostly deals with trap-assisted recombination, implying capture of an electron (or a hole) from the conduction band (or valence band) followed by successive recombination with a hole (or an electron) in the valance band (or conduction band). The associated rate constant $k_{SRH}^c$ (or $k_{SRH}^h$) depends upon the total trap density $N_p$ and capture coefficients $c_p$ (or $c_n$) according to the relation $k_{SRH} = c_p N_p$ where $c_m$ = $\sigma_m (\nu_m^k)$, $\sigma_m$ is the electron (or hole) capture cross section and $(\nu_m^k)$ is the thermal velocity of the charges, given by $(\nu_m^k)$ = $(3k_B T/m_n^k)^{1/2}.^{41}$ Therefore, the SRH recombination rate increases with temperature, in contrast to our results in Figure 2c, where a decrease with temperature is observed above 300 K. The decrease could be because of filling of traps sites at higher temperatures by thermally generated intrinsic charges. These competing processes could give rise to a trend as can be clearly seen for one of the charges in Figure 2c in blue. For the case of the other type of charges, as shown in Figure 2d, the thermally generated intrinsic charges may not simply fill the traps, thus the rate constant does not decrease at higher temperatures. The stretched exponential parameter $\tau_\theta$ is found to be 500 $\pm$ 100 ns, corresponding to a characteristic time scale of 43 $\pm$ 9 meV. It is also observed that the stretched exponential parameter $\theta$ only determine the longer time scale of the conductivity signals in the range of roughly 25–40 ns. The temperature dependence of characteristic trapping rate constant of the charges $k_{SRH}$, as shown in green in Figure 2c, is not very pronounced for one type of charges but strongly thermally activated for the other type of charges in Figure 2d. This is similar to the trends observed for trapping of charges in selenium.

Radiative Yield (RY) of Charges. The radiative yield (RY), by definition, is the ratio of the number of photons emitted from the sample and the net number of electrons and holes annihilated radiatively or nonradiatively equaling the generated charge carrier number. The ratio for the instantaneous radiative yield (RY) is given by

$$\text{RY}(t) = (2k_d[n(t)n(t) - n(t)^2] + n(t)[k_{SRH}^c n(t) + k_{SRH}^h n(t)] + 2k_d[n(t)n(t) - n(t)^2]$$

with $n(t) = (n(t) + \Delta n(t))$. Integrating the numerator and denominator over time yields an estimate for the total (time-integrated) radiative yield (RY), as discussed later. From the theoretical analysis, the 5 ns pulse (peak value in Figure 1a) yields excess densities of electrons and holes equal to density of (3.7 $\pm$ 0.5) $\times$ 10$^{15}$ cm$^{-3}$. To compare the significance of decay, namely, radiative recombination, SRH recombination, and stretched-exponential decay, the instantaneous radiative yield expression can be further rewritten, taking the densities of electrons and holes to be equal, as they fall in the aforementioned uncertainty. This simplification enables direct comparison of the processes in the same units. In such a case, the second-order radiative decay rate can be simplified into $k_{SRH}^c [\Delta n(t) + 2n(t)]$, corresponding to a pseudo-first-order decay with rate $k_{SRH}^c [\Delta n(t) + 2n(t)]$. At room temperature, the obtained value for $k_d$ is (1.1 $\pm$ 0.1) $\times$ 10$^{-8}$ cm$^3$ s$^{-1}$, which yields a value for $k_{SRH}^c$ (at 5 ns) = $k_d [\Delta n(t) = 5 ns] + 2n(t) = (5.8 \pm 0.2) \times 10^3$ s$^{-1}$, whereas for long-time scale, the value is $k_{SRH}^c (t \to \infty) = 2k_d n(t) = (1.78 \pm 0.04) \times 10^7$ s$^{-1}$. Additionally, the room-temperature SRH recombination rate and the characteristic decay rate by stretched-exponential decay are (7.8 $\pm$ 0.47) $\times$ 10$^3$ and (1.0 $\pm$ 0.5) $\times$ 10$^7$ s$^{-1}$, respectively, and hence considerably lower than the number above. Using the values for the decay rate constants, $\Delta n$ (at 5 ns) and eq 6, the obtained value for the instantaneous RY ($t = 5$ ns) is ca. 0.98 (or 98%), which decreases to ca. 0.92 (or 92%) for long-time scale (~40 ns), where most of the pulse-generated charges have decayed.

The total RY is obtained by integrating the numerator and denominator, as shown in the following equation

$$\text{RY} = \int_0^\infty 2k_d[n(t) + \Delta n(t)] \, dt$$

$$+ \int_0^\infty \left[ \frac{2[n(t) + \Delta n(t)]}{(t_{th}^c + t_{th}^h)[n(t) + \Delta n(t)]} + 2k_d[n(t) + \Delta n(t)] \right] \, dt$$

(7)

In the above equation, $\tau_{th}^c$ and $\tau_{th}^h$ are inverse of the corresponding rates $k_{SRH}^c$ and $k_{SRH}^h$.

Equation 7 yields a total RY of 0.98 (or 98%). This result indicates a predominant strong radiative recombination in van der Waals bound chains of Te.

For excess densities of electrons and holes on the order of 10$^{15}$ cm$^{-3}$, the RY is much higher than that for a similar band gap material such as black phosphorus,53 where a comparable RY can be achieved only at an excess density of 10$^{15}$ cm$^{-3}$. The high RY at a density of 10$^{15}$ cm$^{-3}$ together with an appreciably high carrier mobility makes Te a material of high potential in efficient infrared light-emitting diodes or laser diodes.55 Note that a high current is needed in laser diodes to achieve population inversion. On the other hand, it is suitable for very efficient infrared photodetectors with a high bandwidth and a low Johnson noise at high frequency due to appreciably high carrier mobility, as, e.g., in a photoresistor, the noise (voltage) amplitude is proportional to the square root of the inverse mobility via

$$\text{noise} \approx \sqrt{4k_B T R} = 2L \frac{k_B T}{e(n_H^c + n_H^h) + \Delta f}$$

with the detector resistance $R$ of a photodetector of length $L$.26 At low (modulation) frequencies and/or low temperatures, 1/f noise limits the detector performance, resulting in a noise current

$$I_{\text{noise}} = \sqrt{QY R/2h \Delta f},$$

with $P_s$ the infrared signal power, $\Delta f$ the bandwidth, and $h$ the photon energy. From the last equation, it is apparent that a high quantum yield (QY), as measured in Te, is desirable to obtain a high S/N ratio because the signal is proportional to the QY and hence $S/N \propto \sqrt{QY}$. 

845

DOI: 10.1021/jacs.8b09965

Hence, Te is an interesting material for applications due to high quantum yield and appreciably high mobility.

**CONCLUSIONS**

The mobility of charges in Te is thermally deactivated with a room temperature value of 190 ± 20 cm² V⁻¹ s⁻¹. Charges decay with near unity quantum yield via radiative recombination. Te, being a quasi-one-dimensional van der Waals material, has a potential for in-depth studies of interesting optoelectronic properties with isolated atomic chains. Such chains can in principle be obtained by liquid exfoliation, which offers possibilities for large-scale production. Furthermore, the appreciably high mobility and near-unity radiative yield open the potential for applications in nanoelectronics as efficient far infrared detectors with high bandwidth or lasers with high efficiency. Further, far-infrared imaging applications replacing microbolometers may be of interest.

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: p.bhaskar@tudelft.nl (P.B.).
*E-mail: l.d.a.siebbeles@tudelft.nl (L.D.A.S.).

**ORCID**
- Prashant Bhaskar: 0000-0002-5805-9756
- Laurens D. A. Siebbeles: 0000-0002-4812-7495

**Present Address**

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
P.B. and L.D.A.S. thank The Netherlands Organisation for Scientific Research (NWO) for financial support. A.W.A. acknowledges the funding by DFG projects AC290/1-1 and AC290/2-1.

**REFERENCES**